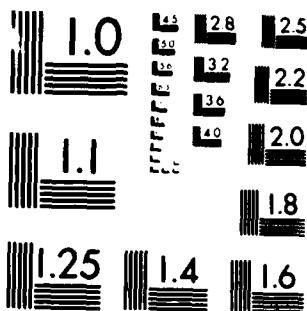


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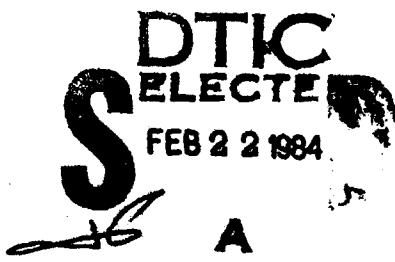
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NRL Report 8779

## High-Temperature Deuterated Lubricants: Additives, Mechanisms, and Methods

JOSEPH E. CAMPANA

*Chemical Diagnostics Branch  
Chemistry Division*

December 30, 1983



NAVAL RESEARCH LABORATORY  
Washington, D.C.

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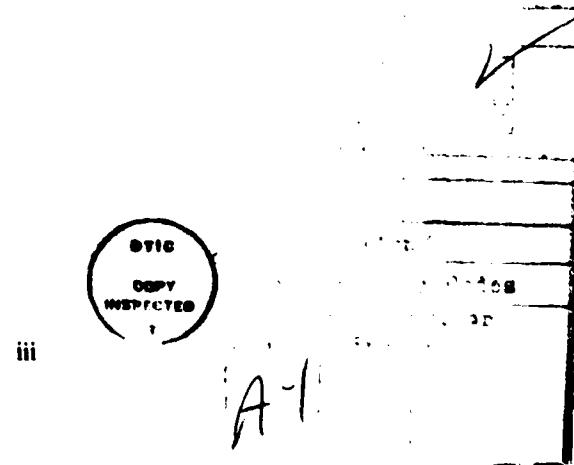
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## EXECUTIVE SUMMARY

Technological advances during the last decade in mechanics, propulsion, and materials have spawned a requirement for thermally and oxidatively stable lubricants having the desirable chemical and physical properties of conventional lubricants such as viscosity, pour point, oiliness, and wettability. The chemistry and engineering of high-temperature lubricant technology has not followed the rapid growth of the mechanical technology, thus application of high-temperature mechanical/material technologies is limited using conventional lubricants. These high-temperature technologies are applicable to a number of areas such as aerospace and marine applications, weapons systems, and public/private transportation. Furthermore, many lubricant applications thought to be moderate temperature processes based on bulk temperature may actually require high-temperature lubricants for increased life performance because of the localized high temperature at the lubricant/surface interface.

High-temperature lubrication impacts the application of advanced technology, energy conservation (reduced friction, Carnot cycle efficiency), reliability (longer bearing/lubricant life), maintenance, economics, and logistics support.

The effect of replacing hydrogen atoms by its stable isotope deuterium on the molecules of lubricant base stocks has been established by the Naval Air Development Center and by NRL. The oxidative stability of the deuterium-enriched base stock is found to be enhanced severalfold relative to the unenriched base stocks. These chemical test data have been corroborated by similar enhancements in the bearing life-performance when the enriched and unenriched lubricants are evaluated in bearing spindle tests. Applied studies are under way at NRL to demonstrate the deuterated lubricant effect in Fleet machinery. The preliminary research and development efforts at NRL on deuterated lubricants have identified several key future research needs required for the effective development of oxidatively stable, high-temperature lubricants.

## HIGH-TEMPERATURE DEUTERATED LUBRICANTS: ADDITIVES, MECHANISMS, AND METHODS

### INTRODUCTION

The requirement for high-temperature, oxidatively stable lubricants has been outstanding in high-technology applications such as aerospace and defense for a number of years. Applicable base fluids such as mineral oils, synthetic hydrocarbons, esters, silicones, fluorocarbons, and polyphenylethers lack at least one important physical property required for high-temperature applications [1], or they have one or more practical limitations such as limited shelf life or corrosiveness. The classes of fluid chemical compounds that have any desirable lubricating properties at elevated temperatures are virtually limited to those mentioned above.

One approach to high-temperature lubricant development requires chemical modification of the best high-temperature fluids to yield advanced high-temperature base fluids. This development must be coupled with a fundamental understanding of the high-temperature chemistry (oxidative and thermal degradation) occurring in the fluid and at the surface/fluid interface in the presence of lubricant additives, as well as the solution chemistry of the additives. This information is required to formulate a high-temperature lubricant that will provide favorable high-temperature chemical dynamics. The development of high-temperature formulations, using high-temperature additives, is the final step in the plan.

### BACKGROUND

In 1975 the Naval Air Development Center (NADC) reported that the replacement of hydrogen with deuterium (heavy hydrogen) on synthetic hydrocarbons resulted in an increased oxidative stability (fivefold determined by chemical methods) and a corresponding increase in the bearing life-performance ratio determined through laboratory-controlled bearing spindle tests [2-4]. It is interesting to note that little improvement in the bearing life-performance ratio was observed until the atom percent deuterium in the hydrocarbon exceeded about 90%. However, a 1:1 mixture of the undeuterated:deuterated (97%) synthetic hydrocarbon material resulted in more than a twofold increase in the bearing life. This result has a direct impact on the cost and benefit of using deuterated base fluids. Figure 1 shows Rebuck and Conte's NADC data.

NRL researchers began investigating the 1975 NADC discovery in the late 1970s with a different chemical class of base fluid. The pentapolyol esters, specifically the pentaerythritol tetraalkanoates, were chosen for study because this class of ester-based fluid has excellent high-temperature properties. Figure 2 shows the model ester, pentaerythritol tetrahexanoate. These ester-based lubricants have been in commercial and military use (MIL-L-23699) as lubricants for gas turbines and precision bearings as early as the 1950s. They have excellent physical properties such as oxidative and thermal stability, a wide operating temperature range (-40° to 400°F), a pour point less than -65° F, a flash point greater than 475°F, and they are compatible with various additives resulting in a long shelf life.

### Preliminary Research

The salient results of one NRL study [5] were:

- The deuterated tetraester lubricant, pentaerythritol perdeuterotetrahexanoate exhibited an impressive oxidative stability compared to the undeuterated analog (fourteenfold) and the synthetic hydrocarbons.

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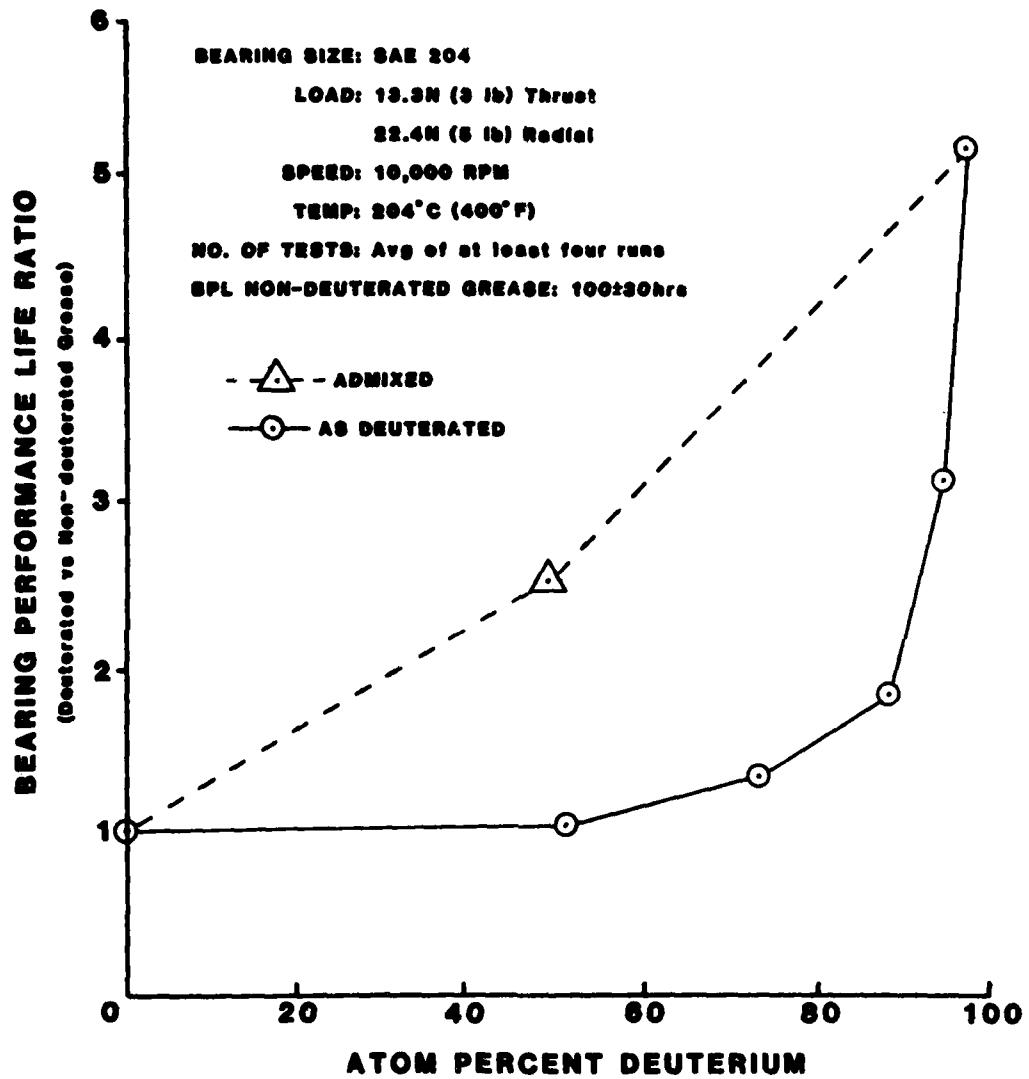


Fig. 1 — Naval Air Development Center — Antifriction bearing performance life ratios of deuterated synthetic lubricants (from Conte, Rebuck et al., Report 77027-30 NADC (1977); *Trans. ASLE*, 69 108 (1977)).

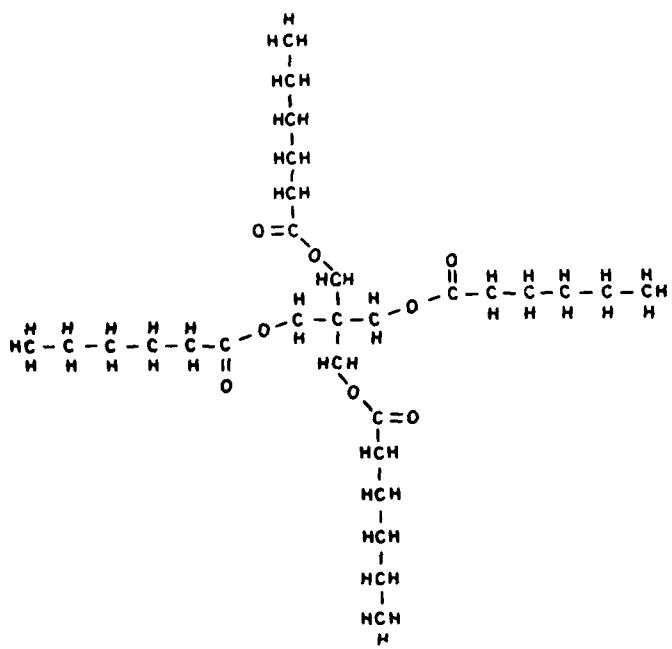


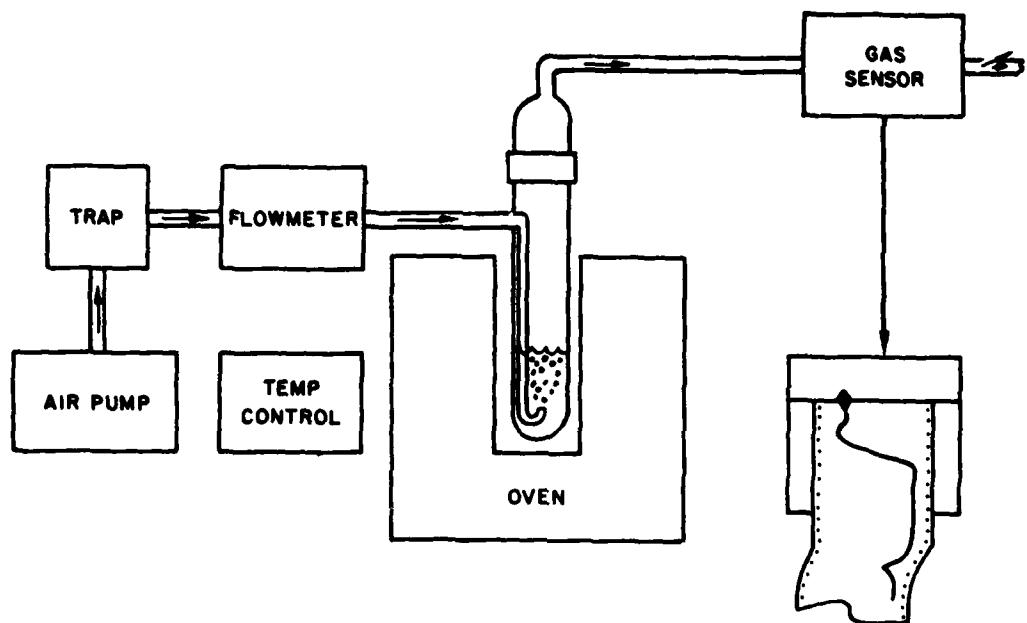
Fig. 2 — Chemical structure of pentaerythritol tetrahexanoate

- The NADC tests were reverified showing that the deuterated synthetic hydrocarbon grease yielded 50 to 240% increase in the bearing life performance over the temperature range 400° to 250°F relative to the undeuterated synthetic hydrocarbon greases.
- A novel oxidative stability test was developed using a solid-state gas sensor (Fig. 3). The gas evolution of a lubricant undergoing oxidation in a heated vessel correlated well with the more classical oxidation indicators such as antioxidant concentration, acid number, and viscosity (Fig. 4).
- An excellent correlation was observed between the synthetic hydrocarbon lubricant oxidative stability (deuterated and undeuterated) determined by a novel NRL gas evolution/gas sensor method [6] and bearing life-performance ratio determined by laboratory spindle tests.
- A cost and benefit analysis of the impact of deuterated fluids on a gyro bearing was impressive but ultraconservative [5]. In 1983 dollars, to remove a system (such as a missile) from service, refurbish it, and put it back into service, would cost from \$20,000 to \$40,000. Typical application of a deuterated lubricant would be about one dollar more than an undeuterated lubricant. Therefore, a modest 50% increase in bearing life would result in a \$1 million to \$2 million savings per year per 100 units, assuming 100 units are refurbished per year.

### Applied Research

A follow-up applied program is currently in progress at NRL whose objective is to extend the life of selected high-failure critical bearings in Fleet auxiliary machinery through the use of deuterated fluids. This program will represent the first application of the deuterated lubricant technology [7]. Progress in this program has led to:

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LUBRICANT OXIDATION RESULTS IN

- VISCOSITY INCREASE
- ANTIOXIDANT DEPLETION
- OXYGEN UPTAKE
- ACIDITY INCREASE
- GAS EVOLUTION
- PEROXIDE FORMATION

Fig. 3 — NRL-developed solid-state gas sensor for oxidative stability tests

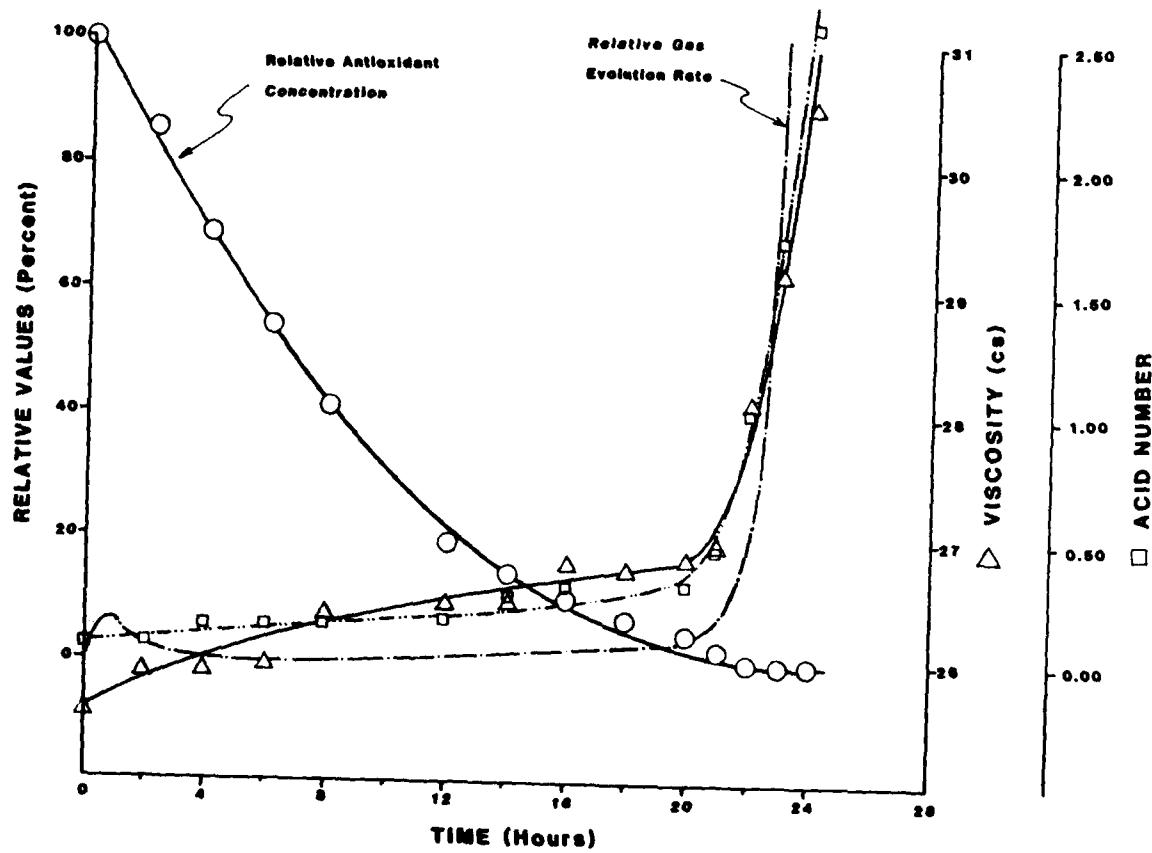


Fig. 4 — Solid-state gas sensor data correlated with classical oxidation indicators

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- The identification of several possible critical naval applications of deuterated lubricants in small bearing systems. For example, in the Naval Sea Systems Command (computer system vacuum blower motors), in the Naval Air Systems Command (Mach Lever Actuator), and in Naval Ordnance Systems Command (missile gyros).
- The establishment of an automated lubricant test facility based on the vacuum blower motors, which can be used as a standard in future tests.
- Pentaerythritol tetrahexanoate-based grease formulations.
- The *rediscovery* of the alkali metal effect [8] to further increase lubricant oxidative stability.
- The observation that minor differences in deuteration (1%) result in dramatic differences in oxidative stability of the ester-based stocks.

The applied program will continue until a statistically significant sample of the conventional lubricant and the deuterated and undeuterated ester-based and synthetic hydrocarbon lubricants are tested. These results will be presented in a future NRL report.

#### Chemical Effects in Lubricants

The research needs to be identified here are concerned with high-temperature lubricants, based on deuterated fluids, and high-temperature additive effects.

#### Deuterium Isotope Effect

The deuterium isotope effect is due to a contribution of three factors (Fig. 5) that make bonds to deuterium less reactive compared to bonds to hydrogen [9].

- A deuterium bond has a lower zero-point energy ( $E_0 = 1/2 \hbar\nu$ ) than a hydrogen bond due to the effect of the difference in mass on the bond-stretching frequencies given by Hooke's law;

$$\nu_H/\nu_D = \sqrt{m_D/m_H} = \sqrt{2} = 1.4,$$

where  $\nu_H$ ,  $m_H$  and  $\nu_D$ ,  $m_D$  are the vibrational frequency and mass of hydrogen and deuterium. There are two consequences to the difference in zero-point energy. Because the zero-point energy of the deuterium bond is lower, the dissociation energy is greater. Similarly, a deuterium-containing compound has a higher enthalpy of activation ( $E_a$ ).

- In absolute rate theory, the rate of reaction is a function of the concentration of the activated complex and its rate of passage over the potential energy barrier. In simplified form, the ratio of the rate constants can be expressed as  $K_H/K_D = e^{(\hbar\nu_H - \hbar\nu_D)/2RT}$ . At high temperature, this expression will approach  $\sqrt{2} = 1.4$ , and the isotope effect will be the greatest at low temperatures.
- Classical statistical mechanics may be used in the treatment of most elements; however, hydrogen should be treated by quantum statistics to allow for its wave nature. With hydrogen there is a possibility for penetration of the potential energy barrier or tunneling. This effect would be less probable for deuterium than hydrogen and would lead to a further difference in the ratio of rates [9].

A. DIFFERENCE IN FREE ENERGY

B. EFFECT OF DIFFERENCE IN MASS ON  
THE VELOCITY OF PASSAGE OVER THE  
POTENTIAL ENERGY BARRIER.

ABSOLUTE RATE THEORY

$$\frac{k_H}{k_D} = e^{(E_a^H - E_a^D)/RT}$$

C. NONCLASSICAL STATISTICS

- CLASSICAL STATISTICAL  
MECHANICS MAY BE USED TO  
TREAT MOST ELEMENTS, INCLUDING  
DEUTERIUM.
- QUANTUM STATISTICS SHOULD BE  
USED TO TREAT HYDROGEN

CONSEQUENCE - HYDROGEN CAN TUNNEL THROUGH THE POTENTIAL  
ENERGY BARRIER.

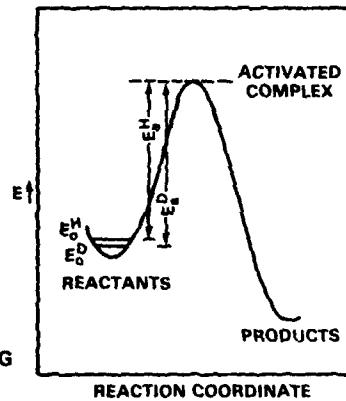


Fig. 5 - Three factors contributing to the lower reactivity of deuterium bonds

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These three factors in combination contribute to the enhanced stability of deuterium bonds over hydrogen bonds; therefore, oxidative stability increases greater than the often assumed factor of  $\sqrt{2} = 1.4$  is not surprising. Also, the bond stability due to isotope effects has been shown to be a function of the chemical environment of the chemically reactive bond [9].

**Additive Effects**

A lubricant additive can be defined as a material that imparts a new and desirable property not originally present in the base fluid, or reinforces a desirable property already possessed by some degree by the base fluid [10]. Table 1 shows the various types of additives mixed with base fluids or stocks to formulate a lubricant. There are many chemical compounds that are effective additives, and many serve more than one of the functions listed in Table 1. The selection of the additive package to formulate a lubricant is empirical. Commercial lubricant formulations are proprietary, which complicates choosing a lubricant for a particular application and the diagnosis of problems or failures.

Table 1 — Types of Lubricant Additives

Antifoam
Antifoulant
Antioxidant
Antisquawk
Antistain
Antiwear
Corrosion Inhibitors
Detergents
Dispersants
Extreme Pressure Additives
Metal Passivators
Pour-Point Depressants
Rust Inhibitors
Synergistic Antioxidants
Thickeners*
Viscosity Index Improvers

\*Required for grease formulations

The effective development of high-temperature lubricants requires a knowledge of the solution-phase and high-temperature chemistry of additive/base stock interactions, additive/additive interactions, and additive/surface interactions. New additives for high-temperature applications may need to be developed, possibly by chemical modification of the most effective conventional additives.

Table 2 shows an example of the effect of lubricant additives on base stock oxidative stability. It also compares various undeuterated ester-based formulations of pentaerythritol tetrahexanoate (PETH) with those of the deuterated hexanoic acid analog, pentaerythritol perdeuterotetrahexanoate (PEdTH). The formulation with a modest percentage of the antioxidant, octyl-PANA, added shows a fourteenfold increase in oxidative stability due to deuteration. The addition of a metal passivator and steel coupon to the formulation preserves the deuterium isotope effect but lowers the actual induction period by more than a factor of two. The addition of 1000 ppm of a sodium complex increases the induction period dramatically (eightyfold) for the undeuterated lubricant, but it decreases the effect of deuteration to sixfold. The addition of a soap thickener (lithium stearate) leaves the deuteration effect unchanged over the use of the sodium complex, but the induction period decreases by a factor of about one-third. Observe that there is almost a 500-fold difference between the extremes of the induction periods of the various formulations shown in Table 2.

Table 2 — Effect of Lubricant Additives on Oxidative Stability

Effect of lubricant additives on the oxidative stability<sup>a</sup> at 428°F of the lubricant based on pentaerythritol tetrahexanoate (PETH) and the deuterated analog (PEdTH) having 98.6 atom percent deuterium in the hexanoic acid moiety.)

Additions to Base Stock	Induction Period (h)		Deuterium Isotope Effect
	PETH	PEdTH	
0.5% octyl-PANA <sup>b</sup>	3, 6	61, 64	14X
1% octyl-PANA	2, 2	28, 24	13X
0.2% BTZ <sup>c</sup>			
Steel Coupon			
1% octyl-PANA	160	965	6X
0.2% BTZ			
Steel Coupon			
1000 ppm Sodium Acetylacetone <sup>d</sup>			
1% octyl-PANA	61	333	5.5X
0.2% BTZ			
Steel Coupon			
11% Lithium Stearate <sup>e</sup>			

<sup>a</sup> Determined using the NRL gas sensor method [6].

<sup>b</sup> Octyl-phenyl- $\alpha$ -naphthylamine (antioxidant)

<sup>c</sup> Benzotriazole (metal passivator)

<sup>d</sup> Synergistic antioxidant

<sup>e</sup> Thickener for grease formulation (possible synergistic antioxidant)

The effect of the alkali metal complex (Li stearate and the Na complex) on the oxidative stability are known to be due to a synergistic antioxidant effect [8]; however, the mechanism of the synergism has not been established. The different alkali metal additives shown in Table 2 also affect the results because the concentrations and the anions and alkali metal identity are different. The effectiveness of the alkali metal has been shown to be  $Rb > K > Na > Li$  [8].

### Conclusions

These preliminary studies demonstrate that the development of advanced high-temperature lubricants requires a detailed understanding of the deuterium isotope effect, the solution chemistry, and the high-temperature chemistry of lubricant systems. The elucidation of the mechanisms of oxidation, thermal or pyrolytic degradation, synergistic antioxidant effects, additive interactions, and surface effects require the application of viable, state-of-the-art analytical techniques and molecular spectroscopy including mass spectrometry and its combined techniques of gas chromatography, liquid chromatography, thermal gravimetric analysis; nuclear magnetic resonance (NMR) spectroscopy, optical spectroscopy, and surface analytical approaches.

The fundamental data obtained by these novel approaches to the study of lubricant chemistry can be used to develop advanced formulations of high-temperature lubricants.

## LUBRICANT RESEARCH

This section presents several research options related to high-temperature, deuterated lubricants. The primary goal of this research is to understand the chemistry of lubricant systems. It is only through a detailed understanding of the chemistry of lubricants that progress can be made in improving lubricant technology.

Some of the options represent innovative approaches to old as well as new problems. These problems and new directions have been identified during recent basic and applied research on deuterated lubricants at NRL. The scope of the options vary in terms of basic and applied research and laboratory experimentation *vs paper studies*. The purpose of the varied options is to provide fundamental and applied chemical, engineering, and logistics data in those areas most critical to the transition of the high-temperature, deuterated lubricant technology and related lubrication technologies to appropriate applications in the Navy, DoD, and the public domain.

### State-of-the-Art Analytical Methods

The elegant mechanistic and kinetic studies such as those described in Refs. 11 and 12 were performed by using laborious classical chemical techniques to study lubricant chemistry. The tedious, time-consuming analytical methods used in such studies limit the number of systems and variables studied; consequently, the technical data base on lubricant chemistry is limited.

The alternative to the classical analytical schemes is state-of-the-art instrumental approaches that may offer the advantage of fast, simple, direct, and *in situ* analysis. We maintain internationally recognized state-of-the-art programs in mass spectrometry, surface science, nuclear magnetic resonance spectroscopy, and laser chemistry. The application of novel diagnostic approaches using these techniques will lag by several years in laboratories currently engaged in lubricant research due to limited resources. The unique situation at NRL could be exploited to investigate the application of state-of-the-art analytical approaches to lubrication chemistry.

It is appropriate to briefly summarize and suggest the novel applications and chemical information that might be obtained by using each of the four instrumental approaches. Many of the following research options will rely on one or more of these methods to study the lubricant chemistry.

#### *Mass Spectrometry*

During the last several years, similarities between solution chemistry and gas-phase ion chemistry have been established with regard to ion solvation effects and acid/base chemistry in aqueous and organic media. Therefore, the study of gas-phase ion/molecule interactions of base stocks and additives by mass spectrometry may bear directly on the lubricant solution chemistry. Gas chromatography (GC), high-pressure liquid chromatography (HPLC), thermal gravimetric analysis (TGA), and chemical reactors coupled directly to the mass spectrometer offer the advantages of speed and direct analysis over off-line methods for the study of oxidation and pyrolysis. Furthermore, the soft ionization methods such as chemical ionization and fast atom bombardment allow easy molecular ion identification in complex mixtures. Mass-analyzed ion kinetic energy spectrometry and other mass spectrometry/mass spectrometry techniques allow the determination of molecular structure (e.g., degradation products) in complex mixtures and the reaction pathways.

#### *Surface Analytical Techniques*

Molecular secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and attenuated total reflectance (ATR) spectroscopy

offer the capability to study the details of base stock/surface chemistry and additive/surface chemistry. Chemisorption, physisorption, and reactions of thin films as a function of temperature can be studied.

#### *Nuclear Magnetic Resonance (NMR) Spectroscopy*

The potential of NMR to study the solution chemistry of simple systems as a function of temperature has not been addressed. For example, the base stock/antioxidant reactions may be studied or the synergistic effect of an antioxidant and antioxidant synergist.

#### *Laser Chemistry*

Surface-enhanced Raman and laser desorption techniques can be used to study lubricant/surface chemistry of thin films. Other laser techniques coupled with mass spectrometry, e.g., laser photodissociation of ions, could be used as a structural diagnostic method.

The development and application of these techniques require the study of known systems followed by the application of the novel instrumental approaches to new systems.

NMR is potentially a powerful analytical tool for the study of lubrication chemistry. For example, various experiments could be performed by using proton NMR. The effect of temperature on deuterated as well as the undeuterated lubricants can be studied. This technique could be used to determine the effect of lubricant additives and how they interact with the base stock. In addition, accelerated aging tests could be performed to predict lubricant shelf life and to study the aging process. Possible ways of extending shelf life could then be determined.

Two novel mass spectrometric approaches that will not only contribute to fundamental studies, but also to the general analysis of lubricant systems for quality assurance, degradation product analysis, and additive component identification in commercial formulations are fast atom bombardment mass spectrometry (FABMS) and combined liquid chromatography/mass spectrometry (LC/MS).

FABMS is an outgrowth of the SIMS approach applied to the study of organic molecular solids as overlayers on metal substrates. There are sample preparation difficulties and bombardment-induced damage of the molecular overlayers in the molecular SIMS approach. The latter difficulty leads to a short-lived molecular ion signal. The dissolution of an analyte in a viscous matrix such as glycerol, the solution of which is then coated on a metal support and subjected to ion or atom bombardment (conventional SIMS analysis), is referred to as FABMS [13]. This technique has a constantly renewed source of sample molecules on the liquid matrix surface due to diffusion of sample molecules to the matrix surface. The technique gives very strong molecular ion signals of labile compounds such as organic salts and organometallic complexes, and for long periods of time. Recently, molecular products from matrix interactions with the solute and solute/solute interactions have been reported [14]. This recent result indicates that solution chemistry can be studied using FABMS. Furthermore, it is generally known in FABMS that preformation of ions in the matrix solution as salts, acids, and bases will result in high abundances of the gas-phase analogs of the solution-phase preformed ions.

A lubricant-base stock is analogous to the liquid matrix used in FABMS, and the additives and degradation products might be considered the analyte species. Therefore, lubricant systems are ideally suited for analysis by FABMS. Figure 6 shows the FABMS spectra of two base stocks, pentaerythritol perdeuterotetrahexanoate (PEdTH), having a low sodium content (<1 ppm), and the same base stock with a high sodium content (2500 ppm). The most intense ion in the mass spectra is due to the loss of one of the perdeuterohexanoic acid moieties at mass-to-charge ratio ( $m/z$ ) 446. The protonated molecular ion at  $m/z$  572 is also observed. The FABMS spectra of the high sodium content fluid shows a strong sodium-PEdTH adduct ion ( $m/z$  595) as well as potassium adduct ions of the major fragment ( $m/z$  486) and molecular ion ( $m/z$  611). These results indicate that:

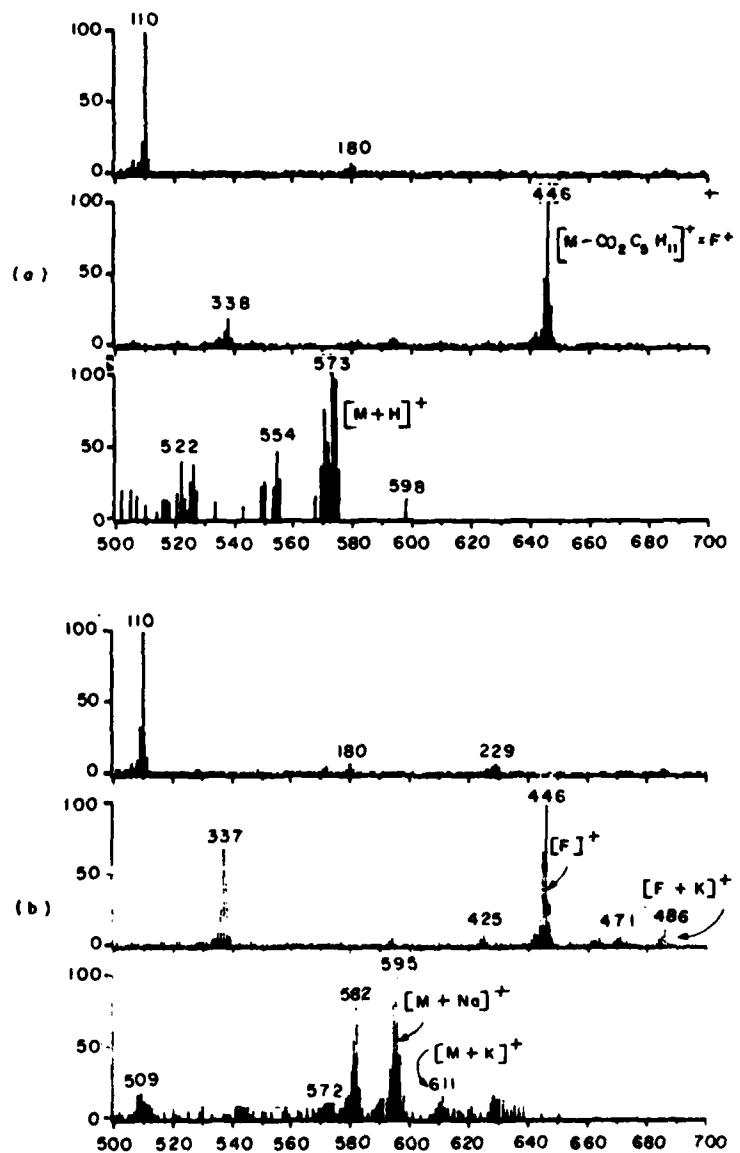


Fig. 6 — Fast atom bombardment mass spectrometry (FABMS) of PEdTH — (a) low sodium content (< 1 ppm) (b) high sodium content (2500 ppm)

- one decomposition product of the PEdTH is due to the loss of the hexanoic acid moiety, which itself may further react and form a hydroperoxy radical, and oxidation initiator, and
- an alkali metal association complex of the PEdTH may exist in solution.

The FABMS method offers considerable potential for the rapid screening of lubricant systems and certainly merits further investigation.

High-pressure liquid chromatography (HPLC) analytically separates thermally labile and involatile materials (e.g., high-temperature compounds). Mass spectrometric detection of the separated components is sensitive and gives an abundance of chemical information. Off-line methods are typically used where prescreened fractions of the HPLC eluate are subjected to conventional mass spectrometric analysis. Several schemes of coupling the HPLC directly to the mass spectrometer have been used over the last decade. These liquid chromatography/mass spectrometry techniques offer many advantages over off-line techniques, but they suffer from technical difficulties. Two new approaches to the LC/MS method offer the use of soft ionization methods. A simple liquid thermal spray method [15] produces ionized solvated and unsolvated species in the beam (spray) production process that apparently are identical to those in solution (Fig. 7(a)). A second method employs a moving belt interface [16] where the HPLC eluate is deposited on a metal belt that moves into the mass spectrometer ion source through special flanges and vacuum pumping, and can be used with various ionization techniques such as electron ionization, chemical ionization, and FABMS. Figure 7(b) shows the HPLC moving belt interface coupled with FABMS previously discussed with the separations capability of HPLC.

The FABMS and LC/MS methods are the most novel of all the techniques discussed, and they have great potential for the study of lubricant chemistry. The ions observed using FABMS [14], the LC/MS thermospray [15], or moving-belt interface [16] may be identical to those in solution.

The general analytical usefulness of these methods will be investigated by studying laboratory-prepared samples of various high-temperature deuterated and undeuterated base stocks with various additives. Additives and species resulting from additive/additive interactions as well as additive/base stock interactions will be identified. These could be studied as a function of temperature with a heated FABMS probe. These experiments will be complemented by off-line experiments where, for example, fractions of sample from an oxidation test are analyzed. Finally, the composition of a commercial base stock such as Herculub-A and its commercial formulation, the undeuterated analog to the NRL pentaerythritol tetraalkanoates, will be studied.

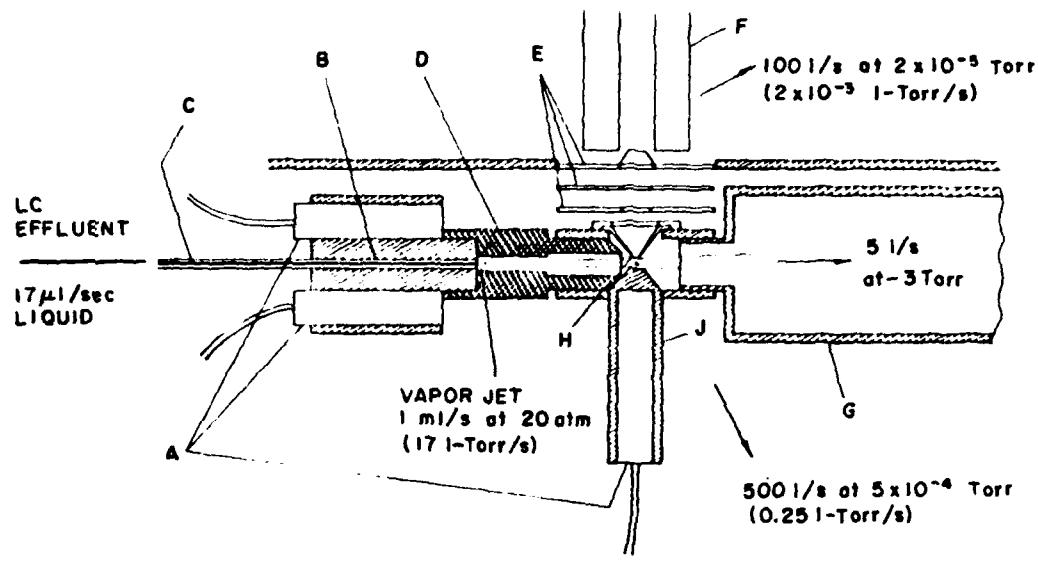
#### Microoxidation/Pyrolysis Analytical Methods

Conventional apparatuses such as the oxygen bomb and heated reactors [6] used for the determination of oxidation and pyrolytic stabilities of lubricants require rather large volumes (>2 mL) of sample. Additionally, some systems cannot be used conveniently with greases. Microtechniques are desirable when evaluating limited amounts of new synthetic base fluids and a variety of their formulations including greases.

One new synthetic method for deuterated materials is currently being investigated at NRL.\* This biotechnology involves the photosynthetic growth of algae in deuterated media, deuterium oxide ( $D_2O$ ), with exposure to carbon dioxide and no hydrogen-containing compounds. The deuterated algae will contain 30 to 40% of deuterated  $C_{16} - C_{18}$  fatty acids, which can be cleaved to an appropriate chain length ( $C_5 - C_{11}$ ) and used as a deuterated alkanoic acid starting material for base fluids such as the pentaerythritol perdeuteroalkanoates. This biotechnological development requires a microanalytical technique to evaluate the stability of the deuterated components of the algae. In this latter case, it is

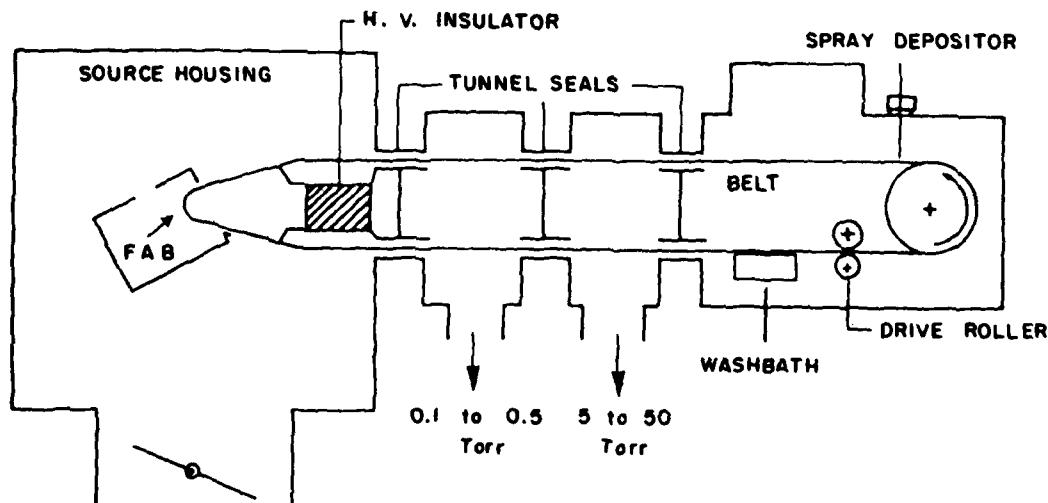
\*These investigations are presently being conducted by Dr. Rex A. Niehof.

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- A. 100-w CARTRIDGE HEATER
- B. COPPER BLOCK BRAZED TO STAINLESS STEEL CAPILLARY;
- C. 1.5 mm OD x 0.15 mm ID SS CAPILLARY
- D. THICK-WALLED COPPER TUBE
- E. ION LENSES

(a)



(b)

Fig. 7 — LC/MS interfaces — (a) thermospray interface (b) moving belt interface coupled to FABMS  
(courtesy of V.G. Analytical Ltd.)

impractical and prohibitive in a research program to produce milliliter quantities of various deuterated components from a variety of microorganisms grown under a variety of conditions.

The FABMS technique requires microliter (1 to 2  $\mu$ L) quantities of material and can be performed on a heated substrate. It is proposed to investigate the FABMS technique as a direct, *in situ*, microoxidation/pyrolysis test to be performed on a heated substrate. Alternately, microoxidation/pyrolysis could be performed exterior to the mass spectrometer, and microliter quantities of sample could be analyzed periodically by FABMS. Oxidation/pyrolysis products will be identified and correlated with degradation by FABMS. Another microoxidation method [17] will be investigated in collaboration with Dr. S. Hsu, Center for Materials Science, Tribocorrosion Group at the National Bureau of Standards (NBS).

FABMS has been used for the direct analysis of peptides as they are produced by the action of proteolytic enzymes on protein and peptide substrates [18]. The FABMS technique potentially could be applied to the direct analysis of deuterated components in microorganisms or various fractions of their cellular components. This latter aspect will be investigated in collaboration at NRL using deuterated and undeuterated organisms, cellular components, and other biological/chemical fractions of the organisms prepared at NRL.

#### **Mechanisms of Oxidation/Pyrolysis**

The previous section discussed the investigation/development of microtests to determine relative oxidation/pyrolytic stabilities. This section, while related, is concerned with elucidating the mechanisms and, if feasible, the kinetics of oxidation and pyrolysis by analytical instrumental methods. The identification of intermediates and their molecular structure are also issues.

These studies will rely on many of the state-of-the-art analytical methods referred to in the corresponding section. Degradation products from a reactor will be monitored as a function of time by various mass spectrometric techniques (GC/MS, LC/MS, FABMS, and NMR). A well-studied system such as the oxidation of pentaerythritol tetraheptanoate [12] will be studied initially, followed by study of the deuterated analog. The results using the new instrumental techniques are expected to give additional information on initiation reactions and the molecular structure and concentration of reactive intermediates. Gas-phase ion/molecule reactions and ion cyclotron resonance mass spectrometry (ICRMS) will be used to study the structure and reactivity of proposed intermediate species. Thermal gravimetric analysis directly coupled to mass spectrometry [19] offers another unique method to study pyrolysis/vaporization phenomena in lubricant systems as a function of temperature and pressure. Studies at reduced pressure are pertinent in aerospace applications where a lubricant may experience the reduced atmospheric pressure of the upper atmosphere and outerspace.

The data obtained from these studies will be useful for determining the role of additives on oxidative stability and designing chemical systems resistive to degradative processes.

#### **Alkali Metal Effect**

Alkali metal compounds are known to be strong synergistic antioxidants especially with amine-type antioxidants in ester-based lubricants [8]. This effect has been observed at NRL when evaluating the oxidative stability of a series of deuterated and undeuterated base stocks from different sources to which octyl-phenyl- $\alpha$ -naphthylamine (PANA) had been added [20]. Dramatic differences in the oxidative stabilities were noted and were determined to be a consequence of two factors. The first was small differences in the atom percent deuterium (i.e., 1 to 2% differences), and the second factor was the presence of varying amounts of sodium in each sample resulting from the synthetic procedure. The use of selected metal salts in certain lubrication applications may allow up to an additional 10% of maximum temperature in oxidation stability by optimal choice of the additives.

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Several mechanisms of the alkali metal synergistic effect have been proposed. They are:

- free radical trapping,
- peroxide decomposition,
- metal deactivation,
- regeneration of the primary antioxidant,
- formation of complexes, and
- inhibition of the initiation step.

The first part of this research involves the determination of the mechanism of synergistic action of the alkali metals with antioxidants. Mass spectrometry will be used to study mechanisms of the synergistic effect in the gas phase by conventional ion/molecule reactions and by reactivity studies using ICRMS. The FABMS and LC/MS techniques will also be used to determine metal-additive/additive and metal-additive/base stock interactions; and metal complex formation. Metal deactivation and surface interactions can be studied using surface analytical techniques, and NMR can be used to identify solution-phase reactions. An undeuterated and deuterated PETH with the primary antioxidant PANA and a synergist such as sodium acetylacetone are proposed for initial study. Once diagnostic information is determined, both the primary antioxidant, the synergist (alkali metal and complexing agent), and the concentrations will be varied systematically to study chemical effects.

The second phase of this research will consider some of the more practical aspects of the alkali metal effect. This encompasses addressing problems related to high-temperature surface deposits, short shelf life due to metal complex precipitates, and the most effective metal additive (metal cation and organic anion) and primary antioxidant system.

Systematic studies using the solid-state gas sensor oxidation test, developed at NRL [5,6] will be used to address questions such as: can an effective concentration of alkali metal be achieved without metal addition due to the ubiquitous nature of alkali metals such as sodium and potassium in metallic materials? Can an effective concentration of alkali metal ever be realized in greases due to the high percentage of alkali metal in thickeners such as soaps and high-temperature metal complexes? If required, samples can be analyzed further by use of the variety of analytical techniques previously discussed.

#### Additive Interactions

There are hundreds of additives used throughout the lubricant industry [21,22]—many additives serving a multipurpose (see Table 1), and many proprietary. The actual effect of one additive on another and the role of an additive or its degradation products on the stability of the base stock, is virtually unknown. It would be a monumental and lifetime effort of any organization to study the myriad of possible additive effects. However, some information is desirable and, in fact, critical to the effective formulation of high-temperature deuterated lubricant systems.

This proposal extends the four preceding research options to additive interactions. A typical formulation of a high-temperature deuterated lubricant for a proposed application will be studied in detail. For example, a simple formulation including the base fluid, an antioxidant, and a metal passivator might be studied initially. This involves the study of the oxidation and pyrolytic stability of each additive in the formulation, the mechanism of the degradation, and the chemical intermediates. The next step is the study of each additive on one another and additive/surface interactions. This information will be used to chemically modify the additives to give desirable high-temperature properties and reaction dynamics.

### Advanced Formulations

A high-temperature deuterated lubricant will be the result of the careful choice of a variety of additives and synergists. A pragmatic approach to formulation can be undertaken to provide some data on deuterated lubricant systems. The desired approach will be to apply the data obtained using the empirical formulation approach with the fundamental chemical data obtained in the preceding five tasks to formulate advanced lubricants.

Oxidative stability testing, physical properties determinations, bearing spindle tests, and blower motor tests will be performed under this task to give the relevant data.

### Friction, Wear, and Corrosion Tests

Oiliness, antiwear, and anticorrosion properties of candidate base stock must be studied. Initially, tests will be performed on various deuterated and undeuterated pentaerythritol tetrahexanoates with various additives in collaboration with NBS. Other candidate base stocks, identified by the fractionation of natural lubricants at NBS, will be deuterated, and the friction, wear, and corrosive properties of the deuterated base stocks will be determined. The NBS tests are microtests, requiring minute quantities of base stock for each test. These tests are ideally suited for exploratory synthetic chemistry operations, where milligram quantities of new base stocks may be synthesized and likewise for natural lubricants produced by the biotechnology effort described in the Microoxidation/Pyrolysis Analytical Methods section of this report.

### Synthetic Methods

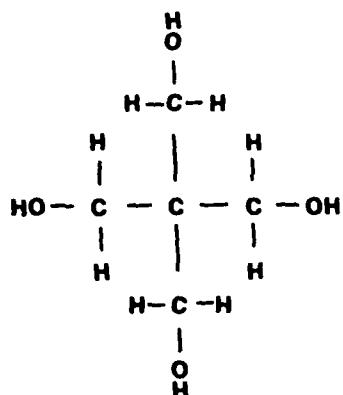
Deuterated base fluids are chemically synthesized by special order through two U.S. and one Canadian chemical specialty house. The synthetic processes are proprietary although they are straightforward from the synthetic chemist's point of view. The actual deuteration of the organic material is the proprietary step and involves cycling the organic material over a catalyst at high temperature in the presence of D<sub>2</sub>O (heavy water). Although the cost of a deuterated lubricant is not prohibitive, especially when viewed on a cost-per-unit basis of relatively small systems, their use in large-scale lubricating oil applications are currently restrictive due to cost.

Figures 8, 9, and 10 schematically describe the synthesis of the deuterated pentaerythritol tetrahexanoate. Figure 8 shows the chemical structure of the two organic starting materials, pentaerythritol and hexanoic acid (its abbreviated structure is shown on the right). It has been shown at NRL [5,11] that most reactive hydrogen bonds are localized on the hexanoic acid portion of the base stock, pentaerythritol tetrahexanoate (Fig. 2). The hexanoic acid is deuterated as shown in Fig. 9 by recycling the hexanoic acid over a hot catalyst in the presence of D<sub>2</sub>O. The atom percent deuterium finally incorporated can vary as a function of procedure and recycle time. Figure 10 shows the reaction that gives the final product. A direct esterification is carried on by refluxing the starting materials, pentaerythritol, and hexanoic acid or perdeuterohexanoic acid in acidic media.

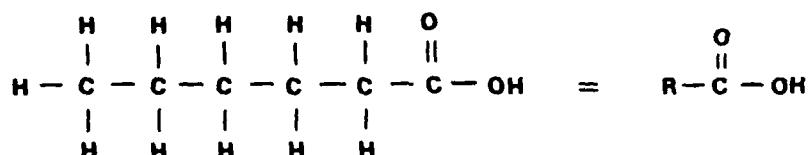
An alternative biotechnological approach under current investigation at NRL was discussed previously. This innovative approach involves the photosynthetic growth of microorganisms in D<sub>2</sub>O in the absence of hydrogen-containing compounds. Deuterated lipids (fatty acids) might be used directly as additives or form the basis for synthetic deuterated organic starting materials. Generally, synthetic methods to deuteration have been neglected by those interested in the science of deuterated lubricants.

The purpose of this task is to survey the literature for feasible synthetic methods for deuteration. Hundreds of catalysts are developed annually, and many of these may have the required activity for selected or complete deuterium exchange reactions. NRL has a catalysis research program that could aid in new synthetic methods. Additionally, an in-house synthetic expertise will be developed.

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## PENTAERYTHRITOL



## HEXANOIC ACID

Fig. 8 - Pentaerythritol tetrahexanoate organic starting materials

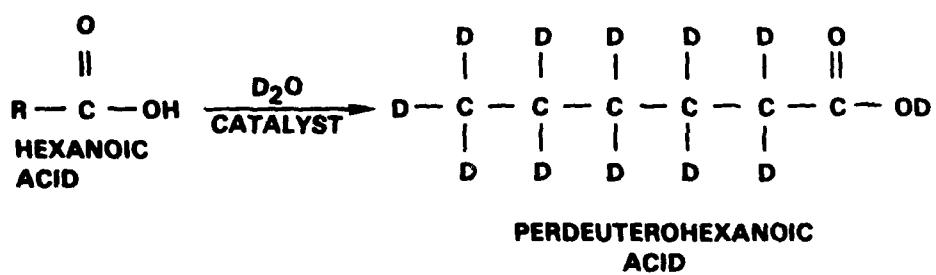
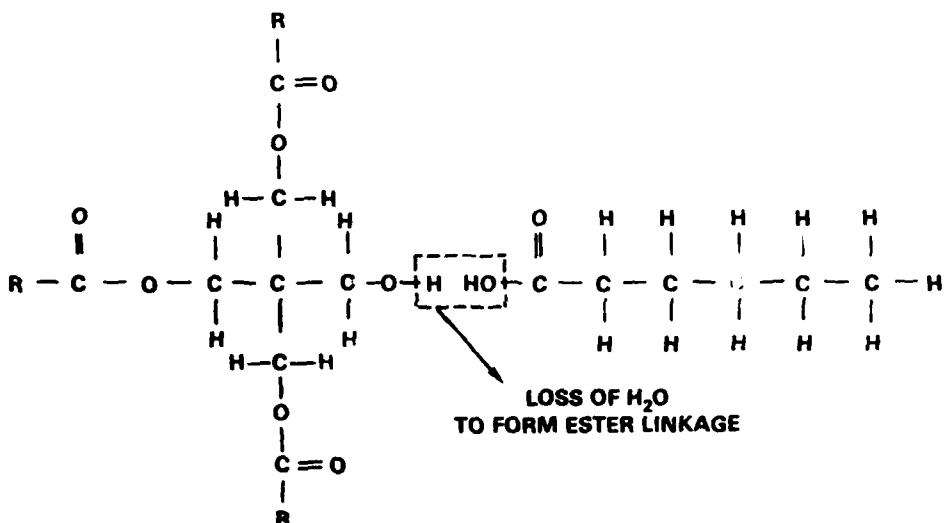


Fig. 9 – Deuteration of hexanoic acid



#### PENTAERYTHRITOL TETRAHEXANOATE

Fig. 10 — Direct esterification of pentaerythritol and hexanoic acid to form the ester pentaerythritol tetrahexanoate

Economic data on the cost of base fluids synthesized from the conventional methods (three commercial sources), biotechnology, and new methods will be determined at the laboratory bench, pilot plant, and full-scale production levels.

#### Applications

Once a specialized high-temperature lubricant is formulated, tested, proven, and generally available, many new high-technology applications will find its use. The more general and immediate concern is, what applications currently exist? Many failures of bearings are found to be material failures rather than lubricant failures, although the failure mode is not easy to determine. It is often difficult to determine whether the bearing or the lubricant failed first without setting up a time-consuming, expensive test program. On the other hand, many lubrication problems can be improved by choice of a different lubricant.

The failure of a lubricant may involve a number of factors such as oxidative and thermal degradation, aging, and other undetermined factors. Many applications thought to be low- or moderate-temperature applications, based on bulk-temperature measurements, may require a specialized lubricant due to high temperatures at the lubricant/surface interface. For example, why do certain high-temperature greases "dry out" in moderate-temperature applications? Does an ABEC-1 bearing operate at higher temperatures (at the bearing/lubricant interface) than an ABEC-9 bearing, and, if so, could life performance be increased with a high-temperature lubricant? The complexity of lubrication engineering limits the studies, data, and answers to all such questions. The basic and applied studies proposed attempt to answer some of these questions.

The transition of technology typically requires many years. The multidisciplinary and basic/applied environment at NRL is conducive to allowing rapid technology transfer. Applications, however, will not come unsolicited to NRL. Consequently, an active search program of candidate-bearing systems must be initiated and ongoing for effective technology transfer. For example, the DoD instrument-bearing working group (IBWG) has issued a list of the national stock numbers of all DoD bearings considered critical. This list could be used as data with a variety of government and DoD

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computerized data bases to find all devices/instruments/machinery using the critical bearings. Each application could then be scrutinized for applicability to the high-temperature deuterated lubricant technology. Other methods include active search at levels from the systems commands to the rework facilities. A few potential Navy applications, mentioned in the introduction, were identified using these various approaches.

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